

**IN THE UNITED STATES PATENT AND TRADEMARK OFFICE**

Applicant: Benazzi et al.

Serial No.: 10/696,548

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Examiner: Singh, Prem, C.

Group Art Unit: 1764

For : FLEXIBLE PROCESS FOR THE PRODUCTION OF OIL BASES AND MIDDLE DISTILLATES WITH A CONVERTING PRETREATMENT STAGE FOLLOWED BY A CATALHYTIC DEWAXING STAGE..

**DECLARATION UNDER 37 C.F.R. §1.132**

Assistant Commissioner for Patents

Washington, D.C. 20231

Sir :

I, Slavik KASZTELAN, being duly warned, declare and say as follows:

THAT, I am a French citizen holding the titles of Engineer delivered by "Ecole des Hautes Etudes Industrielles de Lille" in 1982, of "Docteur ès Sciences" delivered by "Université de Lille" in 1984, of "Doctor accredited to supervise research" delivered by "Université de Lille" in 1991, residing at 69006 Lyon, France, 97 quai Charles de Gaulle.

THAT, I have been engaged on research by "Institut Français du Pétrole" in their Kinetics and Catalysis Department since 1988, where I have been continuously and actively in charge of researches in the fields of hydrocracking, hydroisomerization, dewaxing and hydrogenation of aromatic compounds. I was since September 2002 to April 2006 the manager of the Division "Catalysis and Separation". I am since May 1<sup>st</sup>, 2006, the Assistant Manager of the whole Refining and Petrochemical Division.

I declare further :

THAT, I am familiar with the content of U.S. Patent Application Serial No 10/696,548.

THAT, I declare below the technical reasons supporting the patentability of the claimed invention.

We compare the resulting effects of a process according to the invention using in its converting pretreatment of the feedstock (step a) a catalyst prepared according to the US 4 837 193, with a process according to the invention using in its step a) a silica alumina catalyst of the present invention.

**Step a) : converting pretreatment of the feedstock**

**1) Preparation of the catalyst of step a) not in accordance with the invention (according to US 4 837 193)**

A support according to US 4 837 193 is prepared as follow according to the operating mode described col 7 lines 37 to 63 :

An aqueous solution of an acidic aluminium solution and an alkali hydroxide are added to hot water at 70°C. This solution is kept at a temperature of a 65°C for 2 hours during which an aqueous solution of an alkali silicate and a mineral acid solution are added. The precipitate is filtered, washed with an ammonium acetate, dried at 200°C and calcined at 500°C.

The silica content of the support is 12% by weight.

This operating mode leads to a homogeneous alumina-silica support which is characterized by the presence of a single silico-aluminum zone. The Si/Al ratio measured by MET is constant on the whole zone and is equal to the overall Si/Al ratio that is determined by X fluorescence. The Si/Al ratio is 0,12. The resulting specific surface BET is 263 m<sup>2</sup>/g.

Then the catalyst is prepared according to catalyst X of Example 18 (see col 15-16)

Catalyst X displays 12% by weight of silica, 4% of Nickel and 14% by weight of Molybdenum.

**Preparation of the catalyst C of step a) in accordance with the invention.**

Catalyst C is prepared from a silica-alumina (SA) according to the invention. The aluminum hydroxide powder was prepared according to the process that is described in Patent WO 00/01617. This powder is mixed with a silicic acid solution that is prepared by decationizing resin exchange, then filtered.

This operating mode, mixing an alumina compound that is partially soluble in acid medium shaped with a totally soluble silica compound, leads to a heterogeneous alumina-silica support which is characterized by the presence of two silico-aluminum zones.

The composition of the mixed substrate in anhydrous product is, at this stage, 88%  $\text{Al}_2\text{O}_3$ -12%  $\text{SiO}_2$ . Shaping is carried out in the presence of 15% nitric acid relative to the anhydrous product. The mixing is done in a Z-arm mixing machine. The extrusion is carried out by passage of the paste through a die that is equipped with orifices with diameters of 1.4 mm. The extrudates that are thus obtained are dried at 150°C, then calcined at 550°C, then calcined at 750°C in the presence of water vapor.

The characteristics of the SA substrate are as follows:

The composition of the substrate is 88%  $\text{Al}_2\text{O}_3$ -12%  $\text{SiO}_2$ .

The BET surface area is 268  $\text{m}^2/\text{g}$ .

The total pore volume, measured by nitrogen adsorption, is 0,44  $\text{ml/g}$ .

The mean pore diameter, measured by mercury porosimetry, is 61 Å.

The ratio between volume V2, measured by mercury porosimetry, encompassed between  $D_{\text{mean}} - 30 \text{ Å}$  and  $D_{\text{mean}} + 30 \text{ Å}$ , to the total mercury volume is 0,9.

Volume V3, measured by mercury porosimetry, encompassed in the pores with diameters of more than  $D_{\text{mean}} + 30 \text{ Å}$ , is 0,021  $\text{ml/g}$ .

Volume V6, measured by mercury porosimetry, encompassed in the pores with diameters of more than  $D_{\text{mean}} + 15 \text{ Å}$  is 0,028  $\text{ml/g}$ .

The pore volume, measured by mercury porosimetry, encompassed in the pores with diameters of more than 140 Å, is 0,010  $\text{ml/g}$ .

The pore volume, measured by mercury porosimetry, encompassed in the pores with diameters of more than 160 Å, is 0,009  $\text{ml/g}$ .

The pore volume, measured by mercury porosimetry, encompassed in the pores with diameters of more than 200 Å, is 0,005  $\text{ml/g}$ .

The pore volume, measured by mercury porosimetry, encompassed in the pores with diameters of more than 500 Å, is 0,001  $\text{ml/g}$ .

The B/L ratio of the substrate is 0,10.

The packing density of the catalyst is 1,04  $\text{g/cm}^3$ .

The X diffraction diagram contains at least the characteristic main gamma lines and in particular it contains the peaks at one d encompassed between 1.39 and 1.40 Å and at one d encompassed between 1.97 Å and 2 Å.

The atomic sodium content is 200 +/- 20 ppm. The atomic sulfur content is 800 ppm.

The NMR MAS spectra of the solid of  $^{27}\text{Al}$  of the catalysts show two clusters of separate peaks. A first type of aluminum whose maximum resonates toward 10 ppm extends between -100 and 20 ppm. The position of the maximum suggests that these radicals are essentially of AlVI type (octahedral). A second type of minority aluminum whose maximum resonates toward 60 ppm extends between 20 and 100 ppm. This cluster can be decomposed into at least two radicals. The predominant radical of this cluster would correspond to AlIV atoms (tetrahedral). The proportion of octahedral AlVI is 70%.

The catalyst contains two silico-aluminum zones, whereby said zones have Si/Al ratios that are less than or greater than the overall Si/Al ratio that is determined by X fluorescence. One of the zones has an Si/Al ratio that is determined by MET of 0,57, and the other zone has an Si/Al ratio that is determined by MET of 0,05. The overall Si/Al ratio determined by X fluorescence is 0,12.

Catalyst C is obtained after impregnation of the noble metal on the SA substrate. Platinum salt  $\text{H}_2\text{PtCl}_6$  is dissolved in a solution volume that corresponds to the total pore volume that is to be impregnated. The solid is then calcined for two hours in air at  $500^\circ\text{C}$ . The platinum content is 0.45% by weight. Measured on the catalyst, the BET surface area is equal to 266  $\text{m}^2/\text{g}$ . The dispersion of the platinum that is measured by  $\text{H}_2/\text{O}_2$  titration is 71%.

#### **Preparation of catalyst D.**

We also compare this catalyst according to the present invention with a catalyst D having a support prepared by the same operating mode as in US 4 837 193 col 7 lines 37 to 63, but displaying an active phase based on Platinum. The silica content of the support is 12% by weight.

Catalyst D is obtained by impregnation of the noble metal Pt on the support. the platinum salt  $\text{H}_2\text{PtCl}_6$  is dissolved in a volume of solution corresponding to the total volume pore to impregnate. The solid is then calcined during two hours under  $500^\circ\text{C}$ . The platinum content is 0,45% weight. The specific surface measured on the catalyst is 263  $\text{m}^2/\text{g}$ .

**Evaluation of Catalysts C (in accordance with the invention), X (comparative example : not in accordance with the invention) and D ( not in accordance with the invention) in a Pretreatment Stage of a Hydrotreated Vacuum Distillate followed by a Separation and a catalytic Hydrodewaxing followed by a Separation and a Hydrofinishing Stage.**

To be able to directly use the pretreatment stage catalysts, the feedstock therefore was hydrotreated in advance, and the main characteristics of the feedstock obtained are recorded in Table 1 of the present invention page 65

The operating conditions of step a) are the same as the ones described in example 2 of the present invention.

The net conversions of the feedstock into products that have boiling points of less than 380°C that are thus obtained under these conditions as well as the VI of the 380°C+ fraction (measured after solvent dewaxing at -20°C, by methyl isobutyl ketone (MIBC)), and the pour point of the non-dewaxed 380°C+ fraction are provided in Table 1.

**Table 1**

	1	2	3	4
	Feedstock = Hydrocracking Residue	Stage (a) (Catalyst C Pretreatment Stage)	Stage (a) (Catalyst X Pretreatment Stage) <b>Comparative example</b>	Stage (a) (Catalyst D Pretreatment Stage)
Reaction Temperature °C	/	335	335	335
P Total (bar)	/	120	120	120
Conversion of 380°C-(% by Weight)	/	17	1	12
Sulfur (ppm by weight)	3	/	3	/
Nitrogen (ppm by weight)	1	/	1	/
380°C+ Fraction				
Pour Point (°C)	+42	+38	+42	+39

	1	2	3	4
	Feedstock = Hydrocracking Residue	Stage (a) (Catalyst C Pretreatment Stage)	Stage (a) (Catalyst X Pretreatment Stage) <b>Comparative example</b>	Stage (a) (Catalyst D Pretreatment Stage)
<b>380°C+ Fraction After Solvent Dewaxing (MIBC)</b>	<b>380°C+ Fraction of the Solvent- Dewaxed Hydrocracking Residue</b>	<b>380°C+ Hydroisomerized and Solvent- Dewaxed Fraction</b>	<b>380°C+ Hydroisomerize d and Solvent- Dewaxed Fraction</b>	<b>380°C+ Hydroisomerize d and Solvent- Dewaxed Fraction</b>
VI	105	121	105	115
Pour Point (°C)	-20	-20	-20	-20

These results show that for conversion rates on the order of 30%, it is possible to increase the VI of the 380°C+ fraction (obtained after solvent dewaxing (-20°C) by methyl isobutyl ketone (MIBC). In the case of catalyst C, the gain of VI is 16 points, and in the case of catalyst X the gain is 13 points. By contrast, the pour point of the 380°C+ fraction, as obtained at the end of the catalyst C or X pretreatment stage, was only slightly reduced.

#### **Step b) : Hydrodewaxing**

The pretreated residues (380°C+ fraction) on catalyst C, or X are then dewaxed and hydrofinished as described in example 3 of the present invention.

Hydrodewaxing catalyst C2 comprises a ferrierite zeolite prepared according to the operating mode described in the example 1 of the present invention page 65.

The recovered effluent displays the following characteristics :

**Table 2**

	1	2	3
	Stage (b) (Catalytic Hydrodewaxing on C2 + Catalytic Hydrofinishing) of the 380°C+ Fraction that is Obtained from the Catalyst <b>C</b> Pretreatment	Stage (b) (Catalytic Hydrodewaxing on C2 + Catalytic Hydrofinishing) of the 380°C+ Fraction that is Obtained from the Catalyst <b>X</b> Pretreatment (Comparative)	Stage (b) (Catalytic Hydrodewaxing on C2 + Catalytic Hydrofinishing) of the 380°C+ Fraction that is Obtained from the Catalyst <b>D</b> Pretreatment
<b>380°C+ Fraction After Treatment</b>	<b>Catalytically Hydroisomerized, Dewaxed and Hydrofinished 380°C+ Fraction</b>	<b>Catalytically Hydroisomerized, Dewaxed and Hydrofinished 380°C+ Fraction</b>	<b>Catalytically Hydroisomerized, Dewaxed and Hydrofinished 380°C+ Fraction</b>
VI	122	103	112
Pour Point (°C)	-22	-20	-20

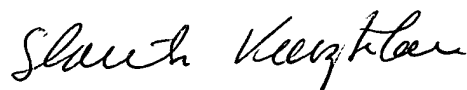
The comparative example demonstrates that the combination of a converting pretreatment stage (step a) using a silica alumina catalyst **C** according to the invention having specific characteristics and an active phase based on noble metal of Group VIII with a catalytic dewaxing stage (step b), leads to higher quality products than a catalyst **X** according to the prior art US 4 837 193.

The comparison of the effect of catalyst **C** and **D** leads to the conclusion that the combination of a converting pretreatment stage (step a) using a silica alumina catalyst according to the invention having specific characteristics and particularly a substrate such that it comprises at least two silico-aluminum zones that have Si/Al ratios that are less than or greater than the overall Si/Al ratio that is determined by X fluorescence, with a catalytic dewaxing stage (step b), leads to higher quality products than the combination of a converting pretreatment stage

using a silica alumina catalyst having homogeneous substrates characterized by the presence of a single silica-aluminium zone.

The undersigned declares further that all statements made herein of this own knowledge are true and that all statements made on information or belief are believed to be true; and further that these statements were made with the knowledge that willful false statements and the like so made are punishable by fine or imprisonment, or both, under Section 1001 Title 18 of United States Code, and that such willful false statements may jeopardize the validity of the application or any patent issuing thereon.

Solaize, January 15<sup>th</sup>, 2007.

A handwritten signature in cursive script, appearing to read "Slavik Kasztelan".

**Slavik KASZTELAN**